Renewable and Sustainable Energy Reviews 14 (2010) 3059–3067

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

A review of thermodynamic cycles and working fluids for the conversion of low-grade heat

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ARTICLE INFO

Article history:
Received 13 May 2010
Accepted 13 July 2010

Keywords:
Organic Rankine cycle
Supercritical Rankine cycle
Organic working fluid
Low-grade heat source

ABSTRACT

This paper presents a review of the organic Rankine cycle and supercritical Rankine cycle for the conversion of low-grade heat into electrical power, as well as selection criteria of potential working fluids, screening of 35 working fluids for the two cycles and analyses of the influence of fluid properties on cycle performance. The thermodynamic and physical properties, stability, environmental impacts, safety and compatibility, and availability and cost are among the important considerations when selecting a working fluid. The paper discusses the types of working fluids, influence of latent heat, density and specific heat, and the effectiveness of superheating. A discussion of the 35 screened working fluids is also presented.

Contents

1. Introduction

Renewable energy sources, such as solar thermal and geothermal, and vast amounts of industrial waste heat are potentially

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doi:10.1016/j.rser.2010.07.006

promising energy sources capable, in part, to meet the world electricity demand. However, the moderate temperature heat from these sources cannot be converted efficiently to electrical power by conventional power generation methods, and a large amount of moderate temperature heat is simply wasted. In this context, research on how to convert these low-grade temperature heat sources into electrical power is of great significance.

Various thermodynamic cycles such as the organic Rankine cycle, supercritical Rankine cycle, Kalina cycle, Goswami cycle, and trilateral flash cycle have been proposed and studied for the conversion of low-grade heat sources into electricity. Although there are broad claims of 15–50% more power output for the same heat input for Kalina cycles relative to organic Rankine cycles, data from actual cycles in operation and simulations under identical conditions of ambient temperature and cooling systems showed that the difference in performance is only 3% in favor of Kalina cycle [1]. However, the organic Rankine cycle is much less complex and need less maintenance.

This review focuses on Rankine cycle derivatives, i.e., organic Rankine cycles and supercritical Rankine cycles. Due to the limitation of the heat source temperature, the influence of the working fluid and the corresponding operating condition can be vital. More than 50 working fluids have been considered in the literature; however, some of them have been rejected due to environmental concerns and their phase out as required by the protocols [2].

The literature shows extensive analyses and comparisons among different thermodynamic cycles and working fluids. However, most of the comparisons were conducted under certain predefined temperature conditions and used only a few working fluids [3–14]. The claims for best working fluids and the cycle with highest efficiencies may not hold true under other operating conditions and among other working fluids.

Instead of suggesting a best working fluid and a best thermodynamic cycle, this paper has reviewed the research on organic Rankine cycles and supercritical cycles, set out the criteria for the selection of working fluids and analyzed the working fluids that have been considered. The results provide insight into the directions of future research on low-grade heat to power conversion, as well as new power plant designs.

In Section 2 of this paper, research on the organic Rankine cycles and supercritical cycles is briefly reviewed and discussed. In order to locate the potential working fluid candidates for the cycles, selection criteria are analyzed and discussed in Section 3. In Section 4, thermodynamic properties of the 35 screened potential working fluids were calculated and tabulated. Based on the selection criteria discussed in Section 3, the screened 35 working fluids were grouped and discussed in Section 5.

2. Review of the organic Rankine cycles and supercritical Rankine cycles

Researchers have proposed and tested variations of Rankine cycles for the conversion of low-grade heat into electrical power and a few cycles have already found their applications [15–17]. But there is still much to learn to improve the performance and bring down the costs. The following is a review of these cycles.

2.1. Organic Rankine cycles (ORC)

The organic Rankine cycle (ORC) applies the principle of the steam Rankine cycle, but uses organic working fluids with low boiling points to recover heat from lower temperature heat sources. Fig. 1 shows a configuration of an ORC, and its processes plotted in a *T–s* diagram. The cycle is configured with an expansion turbine, a condenser, a pump, a boiler and a superheater, provided that superheat is needed.

Pure working fluids used in organic Rankine cycles have been studied, such as HCFC123 ($CHCl_2CF_3$) [3–6], PF5050 ($CF_3(CF_2)_3CF_3$) [4], HFC-245fa ($CH_3CH_2CHF_2$) [18,19], HFC-245ca (CF_3CHFCH_2F) [6], isobutene ($(CH_3)_2C{=}CH_2$) [6], n-pentane [20,21] and aromatic hydrocarbons [22]. Fluid mixtures were also proposed for organic Rankine cycles [23–30]. The organic working fluids have many different characteristics from water [31]. The slope of the saturation curve of a working fluid in a *T–s* diagram can be positive (e.g. isopentane), negative (e.g. R22) or vertical (e.g. R11), and the fluids are accordingly called "wet", "dry" and "isentropic" fluids. Wet fluids like water usually need to be superheated, while many organic fluids, which may be dry or isentropic, do not need superheating. Another advantage of organic working fluids is that the turbine built for ORCs typically requires only a single-stage expander, resulting in a simpler, more economical system in terms of capital costs and maintenance [32].

Different forms of combined systems with organic Rankine cycle as the bottoming cycle were studied [7,33,34], as well as organic Rankine cycle used with different industrial fluids, such as in power plants [7,35–38], desalination [17,39–41], cement industry [42], and the furniture manufacturing industry [43,44]. Technical and economical analyses of the organic Rankine cycle were also carried out [45–48]. Recently, Gerotor and scroll expanders were experimentally tested for performance in organic Rankine cycle [49]. The advantages of ORC over a steam Rankine cycle become obvious for low-grade heat sources when appropriate working fluids and operating conditions are selected [3].

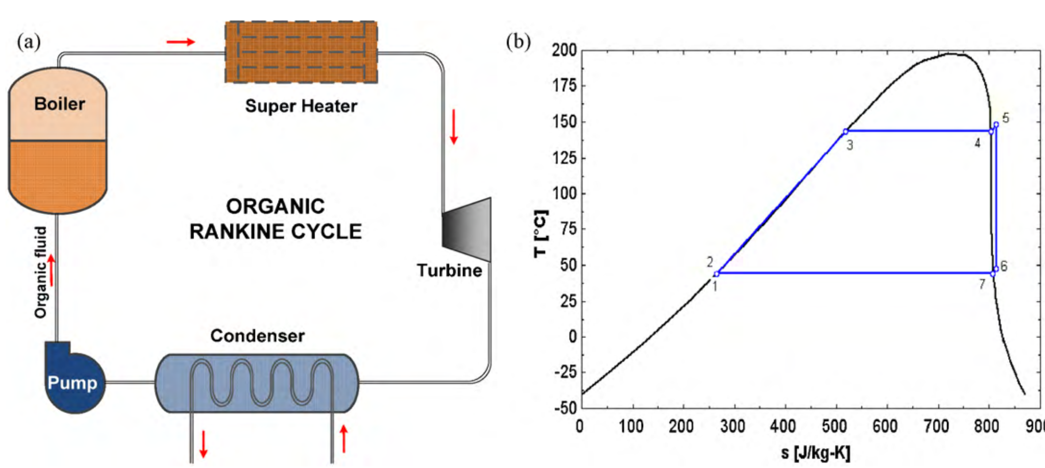


Fig. 1. Demonstration of an organic Rankine cycle. (a) Configuration of an organic Rankine cycle. (b) A organic Rankine cycle process in *T–s* diagram.

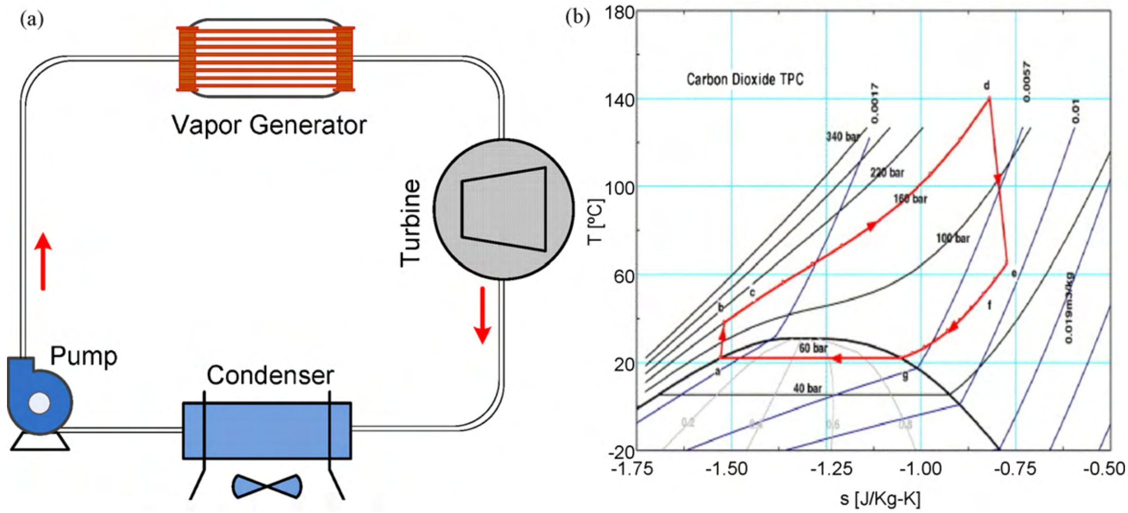


Fig. 2. Configuration and processes of a CO_2 supercritical Rankine cycle. (a) The configuration. (b) The process in a *T–s* diagram (a → b → c → d → e → f → g) [9].

2.2. Supercritical Rankine cycle

Working fluids with relatively low critical temperatures and pressures can be compressed directly to their supercritical pressures and heated to their supercritical state before expansion so as to obtain a better thermal match with the heat source. Fig. 2 shows the configuration and process of a CO_2 supercritical Rankine cycle in a *T–s* diagram [9].

The heating process of a supercritical Rankine cycle does not pass through a distinct two-phase region like a conventional organic Rankine cycle, resulting in a better thermal match in the boiler with less irreversibility. Fig. 3 shows the different thermal matches for R152a in a conventional organic Rankine cycle and R143a in a supercritical Rankine cycle for the same maximum temperature and pinch limitation [50].

Chen et al. [9,51,52] did a comparative study of the carbon dioxide supercritical power cycle and compared it with an organic Rankine cycle using R123 as the working fluid in a waste heat recovery application. Their work shows that a CO_2 supercritical power cycle has a higher system efficiency than an ORC when taking into account the heat transfer behavior between the heat source and the working fluid. The CO_2 cycle shows no pinch limitation in the heat exchanger. Zhang et al. [53–60] have also conducted research on the supercritical CO_2 power cycle. Their experiments revealed that the power generation efficiency was 8.78% to 9.45% [53] and the COP for the overall outputs from the cycle was 0.548 and 0.406, respectively, on a typical summer and winter day in Japan [54]. Organic fluids like isobutene, propane, propylene, difluoromethane and R-245fa [35,61] have also been suggested for supercritical Rankine cycle. It was found that supercritical fluids can maximize the efficiency of the system [35]. However, detailed studies on the use of organic working fluids in supercritical Rankine cycles have rarely been published.

As a working fluid for supercritical Rankine cycle, carbon dioxide has desirable qualities such as moderate critical point, stability, little environmental impact and low cost. However, the low critical temperature of carbon dioxide, 31.1 °C, might be a disadvantage for the condensation process. As we can seen in Fig. 2, carbon dioxide has to be cooled below the critical point (31.1 °C), preferably to around 20 °C in order to condense, which is quite a challenge for the design of a cooling system for many cases. Meanwhile, an operating condition of 60–160 bar is a safety concern. Therefore, new working fluids need to be considered to realize the supercritical Rankine cycle.

In a word, both the organic Rankine cycle and supercritical Rankine cycle have their own advantages. Although the supercritical Rankine cycle can obtain a better thermal match than the organic Rankine cycle, the supercritical Rankine cycle normally needs high pressure, which may lead to difficulties in operation and a safety concern.

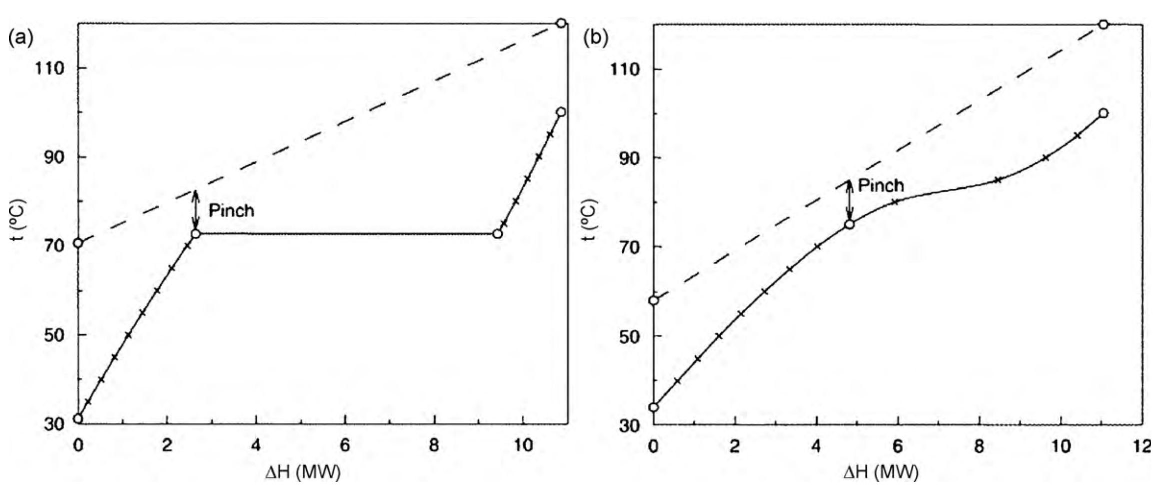


Fig. 3. $T - \Delta\dot{H}$ diagram demonstrating thermal match in an organic Rankine cycle and a supercritical cycle [50]. (a) Heating R152a in a organic Rankine cycle at 20 bar from 31.16 °C to 100 °C. (b) Heating R143a in a supercritical Rankine cycle at 40 bar from 33.93 °C to 100 °C.

3. Working fluid properties and selection criteria

The working fluid plays a key role in the cycle. A working fluid must not only have the necessary thermo-physical properties that match the application but also possess adequate chemical stability in the desired temperature range. The fluid selection affects system efficiency, operating conditions, environmental impact and economic viability. Selection criteria are set out in this section to locate the potential working fluid candidates for different cycles at various conditions.

3.1. Thermodynamic and physical properties

In this section, types of working fluids, fluid density, specific heat, latent heat, critical point, thermal conductivity, specific volume at saturation (condensing) conditions, as well as saturation volumes are analyzed and discussed. The desired properties are then discussed for the screening of potential working fluids.

3.1.1. Types of working fluids

It has been mentioned in Section 2 that a working fluid can be classified as a dry, isotropic, or wet fluid depending on the slope of the saturation vapor curve on a *T–s* diagram (dT/ds). Since the value of dT/ds leads to infinity for isentropic fluids, the inverse of the slope, (i.e. ds/dT,) is used to express how "dry" or "wet" a fluid is. If we define $\xi = ds/dT$, the type of working fluid can be classified by the value of ξ, i.e. $\xi > 0$: a dry fluid (e.g. pentane), $\xi \approx 0$: an isentropic fluid (e.g. R11), and $\xi < 0$: a wet fluid (e.g. water). Fig. 4 shows the three types of fluids in a *T–s* diagram.

Liu et al. derived an expression to compute ξ, which is: [62]

$$\xi = \frac{C_p}{T_H} - \frac{((n \cdot T_{rH})/(1 - T_{rH})) + 1}{T_H^2} \Delta H_H \qquad (1)$$

where $\xi(ds/dT)$ denotes the inverse of the slope of saturated vapor curve on *T–s* diagram, n is suggested to be 0.375 or 0.38 [63], T_{rH} ($=T_H/T_C$) denotes the reduced evaporation temperature, and ΔH_H is the enthalpy of vaporization.

It needs to be mentioned that Eq. (1) is developed through simplifications. The reliability of the equation was verified at the fluids' normal boiling points by Liu et al. [62]. However, our calculations based on the definition of the slope (ds/dT) show that large deviations can occur when using Eq. (1) at off-normal boiling points. Therefore, it is recommended to use the entropy and temperature data directly to calculate ξ if their values are available.

Isentropic or dry fluids were suggested for organic Rankine cycle to avoid liquid droplet impingent in the turbine blades during the expansion. However, if the fluid is "too dry," the expanded

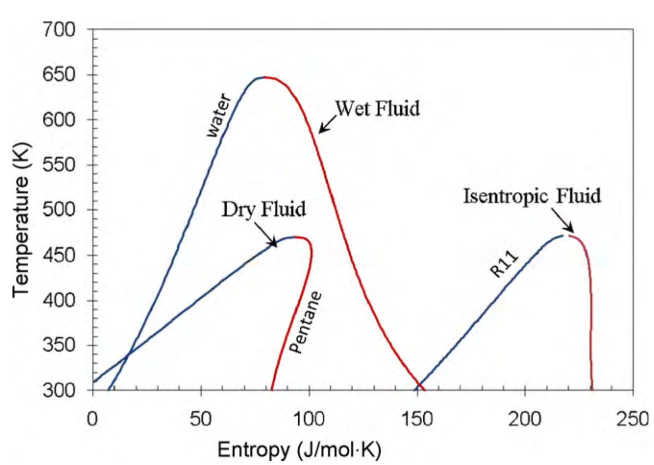


Fig. 4. Three types of working fluids: dry, isentropic, and wet.

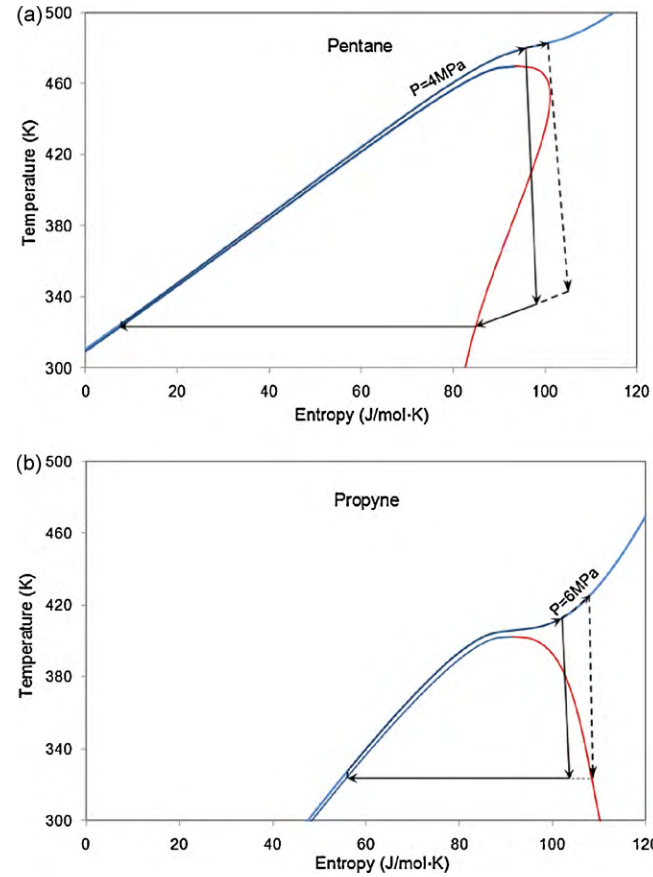


Fig. 5. *T–s* diagram shows a dry fluid and a wet fluid used in supercritical cycles. (a) Pentane as the working fluid. (b) Propyne as the working fluid.

vapor will leave the turbine with substantial "superheat", which is a waste and adds to the cooling load in the condenser. The cycle efficiency can be increased using this superheat to preheat the liquid after it leaves the feed pump and before it enters the boiler. An organic Rankine cycle with an isentropic working fluid is shown in aforesaid Fig. 1(b).

There is still a great need to find proper working fluids for supercritical Rankine cycles. Fig. 5 shows a dry fluid, propyne, and a wet fluid pentane used in supercritical Rankine cycles. If the expansion is carried out such that the expansion does not go into the two-phase region (the dashed lines in Fig. 5(a) and (b)), dry fluids may leave the turbine with substantial amount of superheat, which adds to the burden for the condensation process or a recovery system is needed. Wet fluids, on the other hand, will need higher turbine inlet temperature to avoid two-phase region but there is less concern about desuperheating after the expansion. If the process is allowed to pass through the two-phase region (the solid lines in Fig. 5), the dry fluid can still leave the turbine at superheated state, while the wet fluid stays in the two-phase region at the turbine exit. Bakhtar et al. [64–68] found that for a wet fluid, such as, water, the fluid first subcools and then nucleates to become a two-phase mixture. The formation and behavior of the liquid in the turbine create problems that would lower the performance of the turbine. For dry fluids, Goswami et al. [69] and Demuth [70,71] found that only extremely fine droplets (fog) were formed in the two-phase region and no liquid was actually formed to damage the turbine before it started drying during the expansion. Demuth [70] also found that the turbine performance should not degrade significantly as a result of the turbine expansion process passing through and leaving the moisture region if no condensation occurs. Meanwhile, potential gains in the net fluid effectiveness on the order of 8% can be achieved resulting

from the selection of the turbine expansion process whose equilibrium states pass through the two-phase region. To this end, dry fluids may serve better than wet fluids in supercritical states if the turbine expansion involves two-phase region.

3.1.2. Influence of latent heat, density and specific heat

Maizza and Maizza [23] suggested that high latent heat, high density and low liquid specific heat are preferable, as a fluid with a high latent heat and density absorbs more energy from the source in the evaporator and thus reduces the required flow rate, the size of the facility, and the pump consumption. However, Yamamoto et al. [3] suggested that low latent heat is better because the saturated vapor at the turbine inlet would provide the best operating condition. Here, we conducted a theoretical analysis by deriving the expression of the enthalpy change through the turbine expansion, in order to obtain a comprehensive conclusion.

The transition between the two phases of matter can be characterized by Clausius–Clapayron relation, which is:

$$\frac{dP}{dT} = \frac{L}{T\Delta V} \quad (2)$$

where dP/dT denotes the slope of the coexistence curve on a P–T diagram, L is the latent heat, T is the absolute temperature, and ΔV is the volume change of the phase transition. When the transition is to a gas phase, the specific volume can be many times the size of the initial specific volume, so $\Delta V = V_{gas}$ can be approximated, which is also applied in the current situation.

Here it is assumed that the vapor follows the ideal gas law for the sake of simplification. Since high pressure vapor cannot be considered as an ideal gas, this analysis is only for a qualitative investigation and not meant to do accurate calculations. The ideal gas law is:

$$V_{gas} = \frac{RT}{P} \quad (3)$$

Combining Eqs. (2) and (3) and after integration, the pressure ratio of any two points on the coexistence line of a phase diagram is obtained as:

$$\ln\frac{P_2}{P_1} = \frac{L}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (4)$$

From Eq. (4) one can notice that the pressure ratio of a working fluid is decided by its latent heat when the saturation temperatures are defined.

The unit isentropic enthalpy drop (i.e. the work output) through a turbine is calculated from: [72]

$$\Delta h_{\text{isentropic}} = C_p T'_{\text{in}}\left[1 - \left(\frac{P_{\text{dis}}}{P_{\text{in}}}\right)^{\gamma-1/\gamma}\right] \quad (5)$$

where $\gamma = C_p/C_v$ is the ratio of the heats, T'_{in} is the turbine inlet temperature and P_{dis} and P_{in} denote the turbine discharge and inlet pressures, respectively. The above expression for the enthalpy drop was widely accepted for discussion although it is derived under the assumption of ideal gas with constant specific heats [72,73].

Combining Eqs. (4) and (5) one obtains:

$$\Delta h_{\text{isentropic}} = C_p T'_{\text{in}}\left[1 - e^{L(1/T_1 - 1/T_2)/C_p}\right] \quad (6)$$

where T_1 and T_2 are the saturation temperatures of two points on the coexistence line and $T_1 > T_2$, T'_{in} is the turbine inlet temperature (Fig. 6), and the other notations remain the same.

Eq. (6) shows that fluids with higher latent heat give higher unit work output when the temperatures and other parameters are defined. The influence of the latent heat can also be explained by observing the T–s diagram in Fig. 6. Under defined temperatures, the length of the horizontal line segment is proportional to the latent heat. Long line segment (i.e. latent heat) is expected to obtain large work output because the area formed by the process of the cycle is the work output from the turbine. This result agrees with the conclusion from Eq. (6). Meanwhile, as it has been mentioned, Eq. (6) gives the unit mass work output from the turbine, it can be inferred that fluids with higher density need smaller equipment setup for same power production. In brief, working fluids with high density, low liquid specific heat and high latent heat are expected to give high turbine work output.

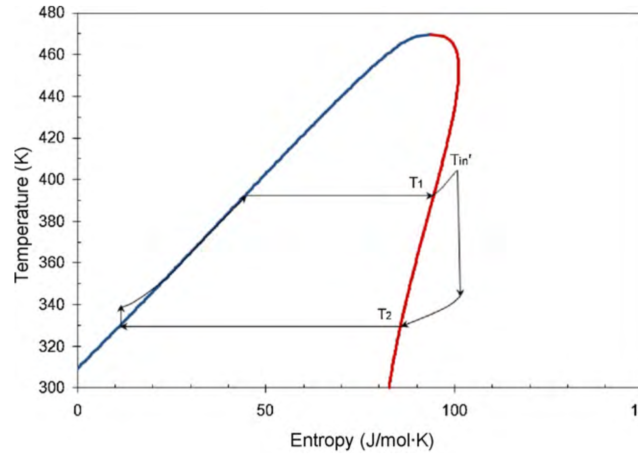


Fig. 6. T–s diagram of an organic Rankine cycle with superheat.

3.1.3. Effectiveness of superheating

A large amount of superheat is used in a traditional steam Rankine cycle to improve the thermal efficiency. However, superheat does not always lead to a higher efficiency for all working fluids. It is the rate at which the constant pressure lines diverge that determines the impact of superheating. For a given incremental increase in the degree of superheat from some reference point, incremental efficiency η' can be defined as the ratio of *incremental* work and heat, shown in Eq. (7) and Fig. 7.

$$\eta' = \frac{\Delta w}{\Delta q} = \frac{\Delta h_1 - \Delta h_2}{\Delta h_1} \quad (7)$$

In order for the cycle efficiency to increase with the degree of superheat, the incremental efficiency must be greater than the efficiency at the reference state (here it is the saturated vapor state). For operation between two isobaric curves, the system efficiency increases for wet fluids while it decrease for dry fluids. The isentropic fluid achieves an approximately constant value for

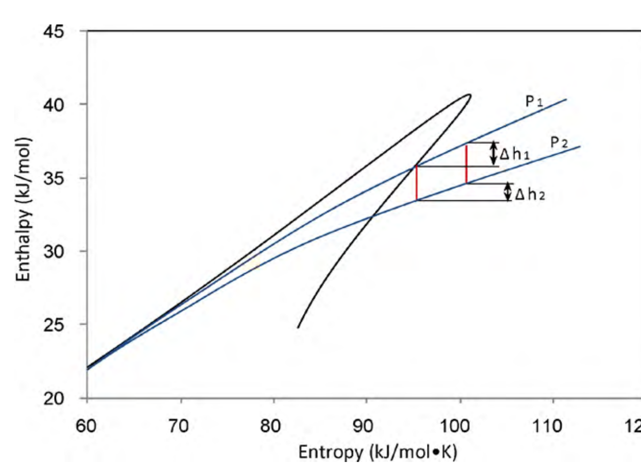


Fig. 7. Enthalpy–entropy diagram of dry fluid pentane demonstrating the effect of superheat.

high turbine inlet temperatures [8]. Based on that, superheat contributes negatively to the cycle efficiency for dry fluids, and is not recommended. For wet fluids, superheat is mostly necessary for turbine expansion safety and improvement of the cycle efficiency.

3.1.4. Critical points of the working fluids

Condensation is a necessary process in the organic Rankine cycle and supercritical Rankine cycle. The design condensation temperature is normally above 300 K in order to reject heat to the ambient; therefore, fluids like methane with critical temperatures far below 300 K are out of consideration because of the difficulty in condensing. On the other hand, the critical point of a fluid considered as the working fluid of a supercritical Rankine cycle should not be too high to overpass. The critical point of a working fluid, being the peak point of the fluid saturation line in a *T*–*s* diagram, suggests the proper operating temperature range for the working fluid of liquid and vapor forms, and the critical temperature is an important data for fluid selection.

Another important thermodynamic property is the freezing point of the fluid, which must be below the lowest operating temperature in the cycle. The fluid must also work in an acceptable pressure range. Very high pressure or high vacuum has a tendency to impact the reliability of the cycle or increase the cost.

3.2. Stability of the fluid and compatibility with materials in contact

Unlike water, organic fluids usually suffer chemical deterioration and decomposition at high temperatures [5]. The maximum operating temperature is thus limited by the chemical stability of the working fluid. Additionally, the working fluid should be non-corrosive and compatible with engine materials and lubricating oil. Calderazzi and Paliano [74] studied the thermal stability of R-134a, R-141b, R-13I1, R-7146 and R-125 associated with stainless steel as the container material. Andersen and Bruno [32] presented a method to assess the chemical stability of potential working fluids by ampule testing techniques. The method allows the determination of the decomposition reaction rate constant of simple fluids at the temperatures and pressures of interest.

3.3. Environmental aspects

As to the environmental aspects, the main concerns include the ozone depletion potential (ODP), global warming potential (GWP) and the atmospheric lifetime (ALT). The ODP and GWP represent substance's potential to contribute to ozone degradation and globe warming. Due to environmental concerns, some working fluids have been phased out, such as R-11, R-12, R-113, R-114, and R-115, while some others are being phased out in 2020 or 2030 (such as R-21, R-22, R-123, R-124, R-141b and R-142b). Those phased-out substances are not included in the following discussion of potential working fluids.

Alternative fluids are being found and applied. The alternatives are expected to retain the attractive properties and avoid their adverse environmental impact. The most promising candidates are still found among fluids containing fluorine and carbon atoms. The inclusion of one or more hydrogen atoms in the molecule, results in it being largely destroyed in the lower atmosphere by naturally occurring hydroxyl radical, ensuring that little of the fluid survives to enter the stratosphere [75].

3.4. Safety

The ASHRAE refrigerant safety classification is a good indicator of the fluid's level of danger. Generally, characteristics like non-corrosive, non-flammable, and non-toxic are expected. But they are not always practically satisfiable or critically necessary. Many substances, like R-601, are considered flammable but this is not a problem if there is no ignition source around. However, auto ignition is a problem, in particular for longer alkanes at temperatures above 200 °C. The maximum allowable concentration and the explosion limit should also be under consideration.

3.5. Availability and cost

The availability and cost of the working fluids are among the considerations when selecting working fluids. Traditional refrigerants used in organic Rankine cycles are expensive. This cost could be reduced by a more massive production of those refrigerants, or by the use of low cost hydrocarbons.

4. Fluid candidates and their properties

Based on these selection criteria and discussion, working fluids can be evaluated by thermodynamic and physical properties, stability and compatibility, environmental impacts, safety, and availability and cost. More than 50 working fluids have been suggested in the literature, among which some have been phased out due to the environmental concerns, and some are not practical for application, such as methane due to their properties.

This paper screened and summarized 35 potential working fluid candidates for organic Rankine cycles and supercritical Rankine cycles, among which water is listed for comparison. Although aspects other than the thermodynamic properties were pointed out in Section 3, they are better off being discussed in engineering design. Important thermodynamic properties of the fluids were calculated and listed, such as molecular weight, critical temperature, critical pressure, critical density, vapor specific heat capacity, latent heat, and ds/dT (see Table 1). It needs to be mentioned that the vapor specific heat capacity C_p, the latent heat L, and the ratio ds/dT are functions of temperature, and the values given in the table are based on 320 K for those whose critical temperatures are above 320 K, because 320 K is the approximate design temperature for condensation. For those fluids whose critical temperatures are below 320 K, it is assumed that the condensation is designed to be at 290 K, and the calculation is based on that.

Multi-component fluids are not included in this study, because the mixing rule is rather complicated and there are numerous combinations. Investigators can still make their own multi-component fluids based on the properties of the pure fluids.

Table 1 is very useful as it suggests how well the substance can serve as a working fluid in an organic Rankine cycle or a supercritical Rankine cycle. The molecular weight suggests the density of the fluid; the critical point suggests the possible operating temperature and pressure range; the turbine work output can be estimated from Eq. (6) with the value of vapor specific heat capacity (C_p) and the latent heat (L); parameter ξ, calculated directly from the definition, describes the fluid type and suggests the effectiveness of superheating.

5. Discussion

There is no best fluid that meets all the criteria discussed in Section 3 for heat sources with different temperatures. Compromise must be made when selecting the fluids. Among all the criteria and concerns, the authors find that the critical temperature and the ξ value are important parameters that suggest which type of cycle a fluid may serve and the applicable operating temperature of the fluid. Thereby, T–ξ charts are introduced in this paper. The screened 35 fluids were distributed in the charts with their critical temperature and ξ value. Fig. 8 is the distribution of the 35 working fluids in a T–$\xi(ds/dT)$ chart, from which the critical temperature

Table 1
Properties of the screened working fluids.

SHRAE number	Name	Molecular weight	T_c (K)	P_c (MPa)	Vapor C_p (J/kg K)	Latent heat L (kJ/kg)	ξ (J/kg K^2)
R-21	Dichlorofluoromethane	102.92	451.48	5.18	339.85	216.17	−0.78
R-22	Chlorodifluoromethane	86.47	369.30	4.99	1069.13	158.46	−1.33
R-23[a]	Trifluoromethane	70.01	299.29	4.83	3884.02	89.69	−6.49
R-32	Difluoromethane	52.02	351.26	5.78	2301.61	218.59	−4.33
R-41[a]	Fluoromethane	34.03	317.28	5.90	3384.66	270.04	−7.20
R-116[a]	Hexafluoroethane	138.01	293.03	3.05	4877.91	30.69	−5.54
R-123	2,2-Dichloro-1,1,1-trifluoroethane	152.93	456.83	3.66	738.51	161.82	0.26
R-124	2-Chloro-1,1,1,2-tetrafluoroethane	136.48	395.43	3.62	908.70	132.97	0.26
R-125	Pentafluoroethane	120.02	339.17	3.62	1643.89	81.49	−1.08
R-134a	1,1,1,2-Tetrafluoroethane	102.03	374.21	4.06	1211.51	155.42	−0.39
R-141b	1,1-Dichloro-1-fluoroethane	116.95	477.50	4.21	848.37	215.13	0.00
R-142b	1-Chloro-1,1-difluoroethane	100.50	410.26	4.06	1036.52	185.69	0.00
R-143a	1,1,1-Trifluoroethane	84.04	345.86	3.76	1913.97	124.81	−1.49
R-152a	1,1-Difluoroethane	66.05	386.41	4.52	1456.02	249.67	−1.14
R-170[a]	Ethane	30.07	305.33	4.87	5264.72	223.43	−8.28
R-218	Octafluoropropane	188.02	345.02	2.64	1244.87	58.29	0.45
R-227ea	1,1,1,2,3,3,3-Heptafluoropropane	170.03	375.95	3.00	1013.00	97.14	0.76
R-236ea	1,1,1,2,3,3-Hexafluoropropane	152.04	412.44	3.50	973.69	142.98	0.76
R-245ca	1,1,2,2,3-Pentafluoropropane	134.05	447.57	3.93	1011.26	188.64	0.60
R-245fa	1,1,1,3,3-Pentafluoropropane	134.05	427.20	3.64	980.90	177.08	0.19
HC-270	Cyclopropane	42.08	398.30	5.58	1911.81	366.18	−1.54
R-290	Propane	44.10	369.83	4.25	2395.46	292.13	−0.79
R-C318	Octafluorocyclobutane	200.03	388.38	2.78	896.82	93.95	1.05
R-3-1-10	Decafluorobutane	238.03	386.33	2.32	928.83	77.95	1.32
FC-4-1-12	Dodecafluoropentane	288.03	420.56	2.05	884.25	86.11	1.56
R-600	Butane	58.12	425.13	3.80	1965.59	336.82	1.03
R-600a	Isobutane	58.12	407.81	3.63	1981.42	303.44	1.03
R-601	Pentane	72.15	469.70	3.37	1824.12	349.00	1.51
R-717	Ammonia	17.03	405.40	11.33	3730.71	1064.38	−10.48
R-718	Water	18.00	647.10	22.06	1943.17	2391.79	−17.78
R-744[a]	Carbon dioxide	44.01	304.13	7.38	3643.72	167.53	−8.27
R-1270	Propene	42.08	365.57	4.66	2387.36	284.34	−1.77
	Propyne	40.06	402.38	5.63	2100.54	431.61	−1.87
	Benzene	78.11	562.05	4.89	1146.72	418.22	−0.70
	Toluene	92.14	591.75	4.13	1223.90	399.52	−0.21

[a] The critical temperature of the fluid is below 320 K, and the data is given based on 290 K.

and the type of each working fluid is shown. Water, toluene, benzene and ammonia are labeled in Fig. 8; the remaining fluids are shown in a close-up look in Fig. 9. The fluids are divided into 5 groups based on their locations in the T–ξ chart and discussed in the following.

5.1. Fluids ammonia, benzene and toluene

It can be observed from Fig. 8 that water is located in the upper left of the chart, which indicates it is the wettest fluid and has the highest critical temperature among all the fluids plotted. These characteristics make it unsuitable for low temperature heat conversion. Ammonia as a deep wet fluid with ξ value of -10.48 J/kg K^2, needs superheating when used in an organic Rankine cycle (here we still call it ORC, although ammonia is not organic). Ammonia is not recommended in supercritical Rankine cycles, since the critical pressure (11.33 MPa) is relatively high. Meanwhile, ammonia is highly hydrophilic, and the ammonia–water solution is corrosive, limiting the materials that may be used.

Benzene and toluene are considered as isentropic fluids with relatively high critical temperatures, which are desirable char-

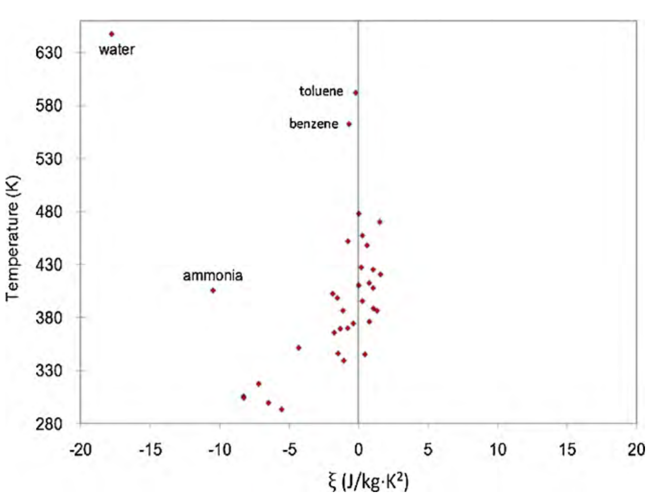


Fig. 8. Distribution of the screened 35 working fluids in T–ξ chart.

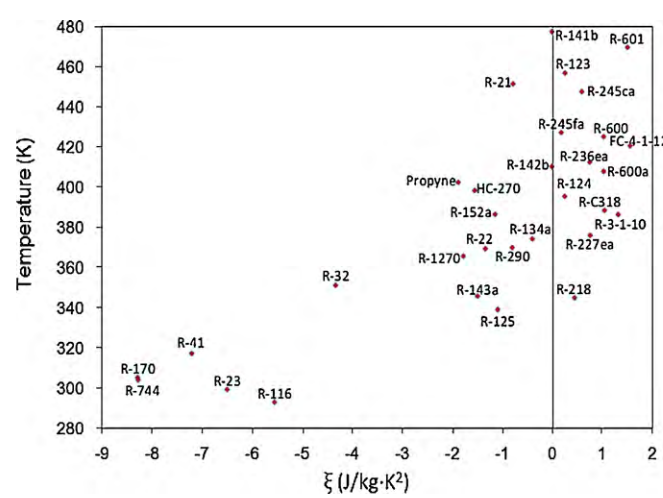


Fig. 9. Close-up look of the distribution of the remaining 31 working fluids in T–ξ chart.

acteristics for organic Rankine cycles. Benzene and toluene are chemically stable in these potential operating conditions [32].

5.2. Fluids R-170, R-744, R-41, R-23, R-116, R-32, R-125 and R-143a

From Fig. 9 it can be observed that fluids R-170, R-744, R-41, R-23, R-116, R-32, R-125 and R-143a are wet fluids with low critical temperatures and reasonable critical pressures (from Table 1), which are desirable characteristics for supercritical Rankine cycles. Carbon dioxide (R-744) and R134a have been studied in supercritical Rankine cycles in the literature. Among these fluids, R-170, R-744, R-41, R-23 and R-116 have critical temperatures below 320 K, which require low condensing temperatures, not achievable under many circumstances. The critical temperatures of R-32, R-125 and R-143a are above 320 K, so the design of condensers for these fluids is not a big concern. Provided other aspects are satisfied, R-32, R-125 and R-143a could be promising working fluids for supercritical Rankine cycle.

5.3. Fluids propyne, HC-270, R-152a, R-22 and R-1270

Propyne, HC-270, R-152a, R-22 and R-1270 are wet fluids with relatively high critical temperatures (Fig. 9). Superheat is usually needed for this group of fluids when applied in organic Rankine cycles. They might be applied in supercritical Rankine cycles if the temperature profile of the heat source meets the requirements. However, propyne, HC-270 (cyclopropane) and R-1270 (propene) are not normally used in their supercritical state due to the stability concerns. Propyne, HC-270 and R-1270 have relatively low molecular weight (Table 1). Applying these fluids implies a larger system size compared to those fluids with higher molecular weight.

5.4. Fluids R-21, R-142b, R-134a, R-290, R-141b, R-123, R-245ca, R-245fa, R-236ea, R-124, R-227ea, R-218

This group of fluids can be considered isentropic fluids (Fig. 9). They can be applied in organic Rankine cycle or supercritical Rankine cycle depending on the temperature profile of the heat source. Since the isentropic expansion would not cause wet fluid problems, superheat is not necessary in organic Rankine cycle with these fluids. Among these fluids, R-141b, R-123, R-21, R-245ca, R-245fa, R-236ea and R-142b have critical temperature above 400 K, making them more likely to be used in organic Rankine cycle than in supercritical cycle for low temperature heat sources, while the rest may be used in either cycle, depending on the heat source profile.

5.5. Fluids R-601, R-600, R-600a, FC-4-1-12, R-C318, R-3-1-10

Fluids R-601, R-600, R-600a, FC-4-1-12, R-C318, R-3-1-10 are considered dry fluids as it can be seen from Fig. 9. Based on the analysis before, dry fluids may be used in supercritical Rankine cycles and organic Rankine cycles. Since superheat has a negative effect on the cycle efficiency when dry fluids are used in organic Rankine cycle, superheating is not recommended. The decision on which fluids could be used may be based on how the operating temperature is tailored to cope with the heat source temperature profile.

6. Conclusion

Organic Rankine cycles and supercritical Rankine cycles were reviewed for low-grade heat conversion into power. Organic Rankine cycles do not have a good thermal match with their heat sources, unlike a supercritical Rankine cycle, but a supercritical Rankine cycle normally needs higher operating pressures.

The properties of the working fluids play vital role in the cycle performance. The thermodynamic and physical properties, stability, environmental impacts, safety and compatibility, and availability and cost are among the considerations when selecting a working fluid. Types of working fluids, influences of latent heat, density and specific heat, and the effectiveness of superheating were discussed in detail. Working fluids with high density and high latent heat provide high unit turbine work output. The study also showed that isentropic and dry fluids are preferred in organic Rankine cycles. Superheating is necessary for wet fluids in organic Rankine cycle. However, for dry fluids superheat could play a negative role in the cycle efficiency. Fluids with low critical temperatures and pressures are potential candidates for supercritical Rankine cycle. Among all the fluids suggested, 35 fluids were screened out, and plotted in the newly introduced T–ξ charts. The fluids were discussed through grouping based on their distributions in the T–ξ chart.

Acknowledgement

The work reported in this paper was funded by the State Florida under the USF-FESC program.

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